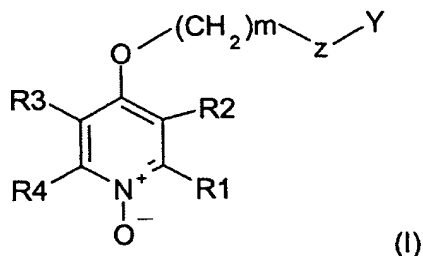


What is claimed is:

1. A process for preparing substituted pyridine N-oxide compounds of the formula

5

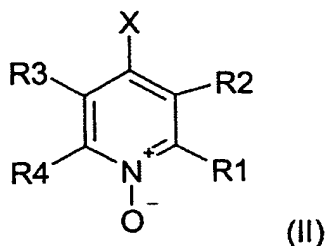


10 in which R1, R2, R3 and R4 are each independently H, a carboxyl group or a C₁-C₁₂-alkyl radical which may optionally contain one or more atoms from the group of N, O and S, or R1 and R2 and/or R3 and R4 together may each form an optionally substituted C₄-C₂₀-alkylene radical which may contain one or more atoms from the group of N, O and S,

15 A is benzyl or a (CH₂)_m group where m may be an integer from 1 to 12, Z₁ and Z₂ are each independently O or S, and Y is H, a C₁-C₁₂-alkyl radical which may optionally contain one or more atoms from the group of N, O and S, a C₆-C₂₀-aryl radical or a C₅-C₂₀-heterocycle,

20 and the radicals may optionally be substituted by halogen, C₁-C₆-alkyl, nitro, phenyl or tert-amine, or Z₂ and Y together may form an optionally substituted ring or an optionally substituted ring system, and the ring or the ring system may

25 contain one or more atoms from the group of N, O and S, from the corresponding 4-halopyridine N-oxide of the formula



in which R1-R4 are each as defined above and X is chlorine, bromine or iodine, which comprises reacting the compound of the formula (II) in the presence of a phase transfer catalyst and of a base with a compound of the formula



in which Z₁, Z₂, A and Y are each as defined above, at a temperature up to the reflux temperature, to give the corresponding substituted pyridine N-oxide compound of the formula (I).

2. The process as claimed in claim 1, wherein compounds of the formula (I) are prepared in which R1, R2, R3 and R4 are each independently H or C₁-C₄-alkyl, A is benzyl or a (CH₂)_m group where m is a number from 2 to 6, Z₁ and Z₂ may each independently be O or S, and Y is H, a C₁-C₆-alkyl radical which may contain one or two atoms from the group of O and S, a C₆-C₁₀-aryl or C₅-C₁₀-heterocycle radical, and the radicals may optionally be substituted by C₁-C₄-alkyl, halogen, nitro, tert-amine or phenyl.

3. The process as claimed in claim 1, wherein the compounds of the formula (II) and of the formula (III) are used in a molar ratio of from 1:1.1 to 1:10.

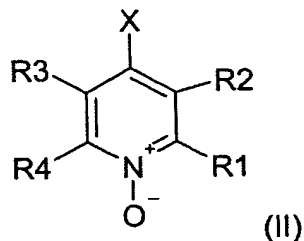
4. The process as claimed in claim 1, wherein the phase transfer catalyst used is an ammonium salt

compound of the formula (V) $R_5R_6R_7R_8N^+A^-$ in which the R_5 to R_8 radicals may each independently be C_1 - C_{20} -alkyl, phenyl, arylalkyl or alkylaryl, and the radicals may optionally be mono- or poly-substituted by functional groups, and A^- is an anion from the group of chloride, bromide, fluoride, iodide, hydroxide, hydrogensulfate, perchlorate, nitrate, acetate, benzoate or mesylate, or is a corresponding quaternary phosphonium salt, polyether of cyclic or acyclic nature, or else an alkyl-substituted guanidinium salt.

5. The process as claimed in claim 1, wherein the phase transfer catalyst used is an ammonium salt compound of the formula (V) $R_5R_6R_7R_8N^+A^-$ in which the R_5 to R_8 radicals are each independently a C_1 - C_{16} -alkyl radical or a benzyl radical, and A^- is a chloride or bromide.

6. The process as claimed in claim 1, wherein the phase transfer catalyst is used in an amount of from 0.1 to 30 mol%, based on the compound of the formula (II).

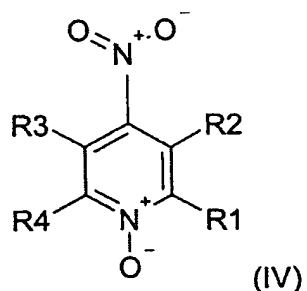
7. A process for preparing a 4-halopyridine N-oxide compound of the formula (II)



30

in which R_1 , R_2 , R_3 and R_4 are each independently H, a carboxyl group or a C_1 - C_{12} -alkyl radical which may optionally contain one or more atoms from the group of N, O and S, or R_1 and R_2 and/or R_3 and R_4

together may each form an optionally substituted C₄-C₂₀-alkylene radical which may contain one or more atoms from the group of N, O and S, and X is chlorine, bromine or iodine, which comprises
5 reacting a 4-nitropyridine N-oxide compound of the formula



10 in which R₁ to R₄ are as defined in formula (II),
in the presence of a phase transfer catalyst and
in the presence of an acid, with an alkali metal
halide to give the corresponding compounds of the
formula (II).

15

8. The process as claimed in claim 7, wherein the
phase transfer catalyst used in the conversion of
the compound of the formula (IV) to the compound
of the formula (II) is an ammonium salt compound
20 of the formula (V) R₅R₆R₇R₈N⁺A⁻ in which the R₅ to R₈
radicals may each independently be C₁-C₂₀-alkyl,
phenyl, arylalkyl or alkylaryl, and the radicals
may optionally be mono- or polysubstituted by
functional groups, and A⁻ is an anion from the
25 group of chloride, bromide, fluoride, iodide,
hydroxide, hydrogensulfate, perchlorate, nitrate,
acetate, benzoate or mesylate, or a corresponding
quaternary phosphonium salt, polyether of cyclic
or acyclic nature, or else an alkyl-substituted
30 guanidinium salt.

30

9. The process as claimed in claim 7, wherein the
phase transfer catalyst used is an ammonium salt

compound of the formula (V) $R_5R_6R_7R_8N^+A^-$ in which the R_5 to R_8 radicals are each independently a C_1 - C_{16} -alkyl radical or a benzyl radical, and A^- is a chloride or bromide.

5

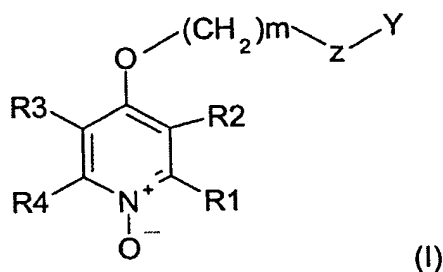
10. The process as claimed in claim 7, wherein the acid used in the conversion of the compound of the formula (IV) to the compound of the formula (II) is HCl, HBr or glacial acetic acid.

10

11. The process as claimed in claim 7, wherein the conversion of the compound of the formula (IV) to the compound of the formula (II) is carried out in a solvent from the group of the optionally halogenated hydrocarbons, ethers and nitriles.

15

12. A process for preparing substituted pyridine N-oxide compounds of the formula



20

in which R_1 , R_2 , R_3 and R_4 are each independently H, a carboxyl group or a C_1 - C_{12} -alkyl radical which may optionally contain one or more atoms from the group of N, O and S, or R_1 and R_2 and/or R_3 and R_4 together may each form an optionally substituted C_4 - C_{20} -alkylene radical which may contain one or more atoms from the group of N, O and S,

25

A is benzyl or a $(CH_2)_m$ group where

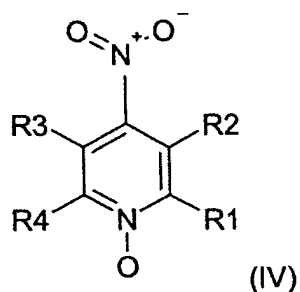
30

m may be an integer from 1 to 12,

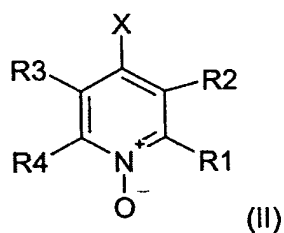
Z_1 and Z_2 are each independently O or S, and Y is H, a C_1 - C_{12} -alkyl radical which may optionally contain one or more atoms from the group of N, O

and S, a C₆-C₂₀-aryl radical or a C₅-C₂₀-heterocycle,
and the radicals may optionally be substituted by
halogen, C₁-C₆-alkyl, nitro, phenyl or tert-amine,
or Z₂ and Y together may form an optionally
substituted ring or an optionally substituted ring
system, and the ring or the ring system may
contain one or more atoms from the group of N, O
and S,

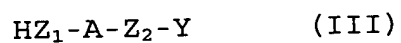
which comprises reacting a 4-nitropyridine N-oxide
compound of the formula



in which R1 to R4 are each as defined in formula
(I), in the presence of a phase transfer catalyst
and in the presence of an acid, with an alkali
metal halide to give the corresponding compounds
of the formula



in which R1 to R4 are each as defined in formula
(I) and X is chlorine, bromine or iodine, and then
afterwards, after isolating it from the reaction
mixture, reacting the compound of the formula
(II), in the presence of a phase transfer catalyst
and of a base, with a compound of the formula



5 in which Z_1 , Z_2 , A and Y are each as defined above,
at a temperature up to the reflux temperature, to
give the corresponding substituted pyridine N-oxide
compound of the formula (I).